



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> : <b>A61K 7/32</b>	<b>A1</b>	(11) International Publication Number: <b>WO 00/61094</b> (43) International Publication Date: <b>19 October 2000 (19.10.00)</b>
<p>(21) International Application Number: <b>PCT/GB00/01230</b></p> <p>(22) International Filing Date: <b>31 March 2000 (31.03.00)</b></p> <p>(30) Priority Data: <b>9908223.2</b>      <b>12 April 1999 (12.04.99)</b>      <b>GB</b></p> <p>(71) Applicant (for AE AU BB CA CY DM GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZA ZW only): <b>UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).</b></p> <p>(71) Applicant (for all designated States except AE AU BB CA CY DM GB GD GH GM IE IL IN KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZA ZW): <b>UNILEVER NV [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).</b></p> <p>(71) Applicant (for IN only): <b>HINDUSTAN LEVER LIMITED [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Mumbai 400 020, Maharashtra (IN).</b></p>		<p>(72) Inventors: <b>ESSER, Isabelle, Claire, Helene, Marie; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). FRANKLIN, Kevin, Ronald; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). GRAINGER, Lynda; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). KOWALSKI, Adam, Jan; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). ROWE, Kathryn, Elizabeth; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB).</b></p> <p>(74) Agent: <b>BAKER, Colin, J.; Eric Potter Clarkson, Park View House, 58 The Ropewalk, Nottingham NG1 5DD (GB).</b></p> <p>(81) Designated States: <b>AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</b></p> <p><b>Published</b> <i>With international search report.</i></p>
<p>(54) Title: <b>ANTIPERSPIRANT COMPOSITIONS</b></p> <p>(57) Abstract</p> <p>An antiperspirant composition is a structured emulsion of a continuous phase containing water-immiscible liquid carrier plus a structurant, and a disperse phase which is a solution of antiperspirant active in water or a mixture of water and water-soluble solvent. The structurant is a fully or partially esterified saccharide. The compositions give low visible residue when applied to skin or to clothing.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Larvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

ANTIPERSPIRANT COMPOSITIONSFIELD OF THE INVENTION

The present invention relates to antiperspirant  
5 compositions with sufficient rigidity to sustain their own  
shape. The usual form of such compositions is a stick.

BACKGROUND OF THE INVENTION

Topically applied antiperspirant compositions are in  
10 widespread use throughout much of the world, in order to  
enable their users to avoid or minimise wet patches on their  
skin, especially in axillary regions. Antiperspirant  
formulations have been applied using a range of different  
applicators depending on the individual preferences of  
15 consumers, including aerosols, roll-ons, pump sprays, sticks  
and so-called mushroom applicators which are used to apply  
cream formulations. In some parts of the world, sticks are  
especially popular. The term stick traditionally indicates  
a bar of material with a solid appearance which was usually  
20 housed within a dispensing container and which retains its  
structural integrity and shape whilst being applied. When a  
portion of the stick is drawn across the skin surface a film  
of the stick composition is transferred to the skin surface.  
Although the stick has the appearance of a solid article  
25 capable of retaining its own shape for a period of time, the

material usually has a structured liquid phase so that a film of the composition is readily transferred from the stick to another surface upon contact. More recently, the term "stick" has been loosely applied to soft solids, which  
5 have a solid form during storage, but which flow under mild pressure or shear, so that in use they can be extruded through an aperture or apertures onto a dispensing surface.

Antiperspirant sticks have been made with a variety of  
10 different types of composition. Suspension sticks contain a particulate antiperspirant active suspended in a structured carrier material which may well be anhydrous. Solution sticks have the antiperspirant active dissolved in a structured carrier which is polar and may be aqueous or may  
15 be based on a non-aqueous polar solvent such as ethanol. A third form of stick is an emulsion of two phases where the continuous phase is structured so that the composition is able to sustain its own shape, the antiperspirant active being dissolved in the more polar of the two phases present.  
20 In some emulsion sticks the antiperspirant active is dissolved in an aqueous disperse phase so that the composition can be classified as a water-in-oil emulsion. The classification into suspension, emulsion and solution types can be applied to both firm and soft solid  
25 compositions.

There is substantial literature on the structuring or thickening of antiperspirant compositions which is frequently accomplished using some form of thickening agent as part of the composition.

5

It has been common practice for sticks to be structured by incorporating fatty alcohol and/wax into the composition. Sticks which are structured with fatty alcohol or wax tend to leave visible white deposits on application to human skin. 10 These deposits can also transfer onto clothing when it comes into contact with the skin and the wearer can, for example, find white marks on the armhole of a sleeveless garment.

There have been some disclosures of antiperspirant stick 15 compositions where structuring to a shape-sustaining stick has been accomplished without using a fatty alcohol or wax. Amongst these disclosures there has sometimes been recognition that white deposits are avoided.

20 Structuring a stick by the incorporation of a thickening polymer has been disclosed in a number of documents including US 5500209, US 5783657 and WO 99/06473.

A class of polymers which has been used in this way is 25 the polyamides. Compositions in this way tend to have poor

sensory properties experienced by the user, notably a sticky or rubbery feel as they are applied.

In some cases structuring has been achieved by the  
5 incorporation of a structurant (also referred to as a gellant or gelling agent) which causes the liquid to gel upon cooling from an elevated temperature. Gel formation takes place as an exothermic event within a temperature range referred to as the gel point; upon reheating, melting of the gel takes place  
10 as an endothermic event within a temperature range. Such gels can be disrupted by shearing and do not recover their structure for a long time, if at all unless remelted, although a small partial recovery may be observed.

15 Some of the prior disclosures are concerned with antiperspirant sticks which contain the antiperspirant active in solid form as a suspension. Thus US-A-5480637 discloses the preparation of an antiperspirant stick in which a suspension of solid, encapsulated aluminium chlorohydrate  
20 dispersed in silicone oil is gelled with 12-hydroxy stearic acid used jointly with a small amount of an alkyl methyl siloxane polymer. US-A-5492691, US-A-5455026 and EP-A-616842 are somewhat similar but do not require the siloxane polymer.

25 US-A-5429816 discloses an antiperspirant stick in which

a solid antiperspirant active is dispersed in a carrier mixture of silicone and other oil which is gelled with 12-hydroxy stearic acid used jointly with n-acyl-amino acid amide. The deposit on skin is said to be a low visible residue, rather than an opaque white deposit. A number of other documents provide similar disclosures of suspension sticks structured with these materials.

US-A-4948578 discloses transparent antiperspirant sticks formed as emulsions where the aqueous phase contains a large proportion of nonionic surfactant as well as water and dissolved antiperspirant active.

Compositions with high viscosity but without gelling or structuring agent are also disclosed in US 4673570 and US 5587153. These compositions are believed to take the form of creams or soft gels which are extruded from a suitable package by the user.

Some prior documents disclose compositions in which two phases are present as an emulsion or teach processes in which two phases are prepared separately and then mixed together. Thus, US 4722835 discloses the incorporation of dibenzyl monosorbitol acetal into sticks prepared by mixing two phases where one phase contains the very polar solvent, propylene

carbonate as well as the DBMSA gelling agent while the other phase contains a large proportion of anhydrous ethanol in which the antiperspirant active is dissolved.

5           US 4265878, US 4725431, US 4719103 and US 4704271 disclose antiperspirant stick compositions in which a solution of antiperspirant active in aqueous solution is dispersed in a hydrophobic continuous phase of hydrocarbon or silicone oil. This hydrophobic continuous phase is  
10 structured to provide a rigid stick by the incorporation of a substantial amount of waxy material, such as stearyl alcohol or spermaceti wax.

          US 4822602 exemplifies a composition structured with  
15 sodium stearate which restricts the choice of antiperspirant active to an unusual active which does not precipitate as an insoluble salt on contact with stearate, but is of poor efficacy. The sodium stearate causes phase transfer of a water-miscible constituent. A stick prepared in accordance  
20 with this example was found to have a tacky, draggy feel on handling.

          US 4719102, US 4725430, US 5200174 and US 5346694 all disclose sticks formed by mixing two phases both of which  
25 contain a substantial amount of a polar solvent. One



contains DBMSA or a similar compound as a structurant while the other phase contains the antiperspirant active dissolved in an alcohol solution with little water present. The alcoholic phase generally contains ethanol or a mixture of  
5 ethanol and propylene glycol.

US-A-5455026 (Bahr) discloses and exemplifies gels of silicone oil containing 12-hydroxystearic acid - frequently in rather small amounts - together with a particulate  
10 antiperspirant active. A further possibility which is mentioned but never exemplified is that the antiperspirant active may be present in solution in an organic solvent. Ethanol and propylene glycol are mentioned as possibilities. This document states that clear gels may be obtained by  
15 matching the refractive index of the antiperspirant to that of the silicone oil.

Formulating a stick to contain substantial amounts of polar organic solvent has associated disadvantages. If the  
20 polar solvent is volatile, like ethanol, the stick gives a cooling sensation when applied. Some cooling may be desired but too much may prove unacceptable to consumers. Polar but less volatile solvents such as water-immiscible diols tend to make a stick feel tacky when touched and hence give a  
25 sensation of stickiness and drag when applied to skin.

Although some of the above mentioned documents disclose emulsion sticks, the marketplace has avoided them.

Antiperspirant stick products currently on the market are either suspension sticks in which the antiperspirant active  
5 is dispersed in particulate form or are solution sticks in which the antiperspirant active is dissolved in a structured single phase which may be transparent but tends to feel tacky or draggy when applied to the skin.

10 Fatty acyl amino acid amides, 12-hydroxy stearic acid and dibenzylidene sorbitol are all examples of compounds which are able to gel and hence structure at least some hydrophobic, water-immiscible organic liquids, although  
dibenzylidene sorbitol will not structure an organic liquid  
15 if an acidic aqueous phase is present, because it will be hydrolysed rapidly. We now believe that they function by forming a network of fibres which appear to be branched or interconnected, and which extend throughout the liquid and thereby give it rigidity. When the gel melts these fibres  
20 dissolve in the liquid.

#### SUMMARY OF THE INVENTION

The present invention is concerned with antiperspirant  
25 compositions which are structured emulsions where the

continuous phase is hydrophobic and the disperse phase is more polar and is a solution of the antiperspirant active in an aqueous solvent.

5        We have found that such compositions can be structured with one or more materials which form a network of fibres in the hydrophobic continuous phase.

Such compositions have the advantage that the deposit on  
10 skin or on clothing (to which material may accidentally be applied) is inconspicuous, in contrast with highly visible opaque deposits from some known compositions.

With suitable choice of materials and proportions it is  
15 possible to achieve other advantages, notably

- satisfactory hardness of the composition,
- satisfactory sensory perception when applied to the skin by the user.

20        In a first aspect this invention provides an antiperspirant composition which is a structured emulsion comprising

i) 15 to 75% by weight of a continuous phase containing water-immiscible liquid carrier and at least one gel-  
25 forming structurant therein,

ii) 25 to 85% by weight of a disperse phase which is a solution of antiperspirant active in water, optionally including water-soluble solvent, wherein said at least one structurant has a molecular weight of less than 10000, provides a network of fibres in the liquid carrier and is present in an amount which is from 1% to 20%, preferably 1% to 15%, by weight of the antiperspirant composition.

10 The structurant serves to gel the continuous phase giving it an increased viscosity or even rigidity. When used in a sufficient amount, not exceeding 15% of the total composition, it is able to structure the composition with sufficient rigidity to sustain its own shape, at least for a  
15 limited time.

It is believed that the fibres or strands of structurant exist as a network extending throughout the water-immiscible continuous phase. These fibres or strands appear to be  
20 branched or interconnected. Upon heating the gel to the gel melting temperature, the strands of structurant dissolve in the liquid phase.

Preferred within this invention are compositions which  
25 have sufficient rigidity that they can be regarded as firm

solids. The hardness of such compositions can be measured with a penetrometer, in a manner which will be described in greater detail below.

5 In order to promote good sensory properties at the time of use it is preferred to include silicone oil in the water-immiscible carrier liquid. The amount of silicone oil may be at least 10% by weight of the composition and/or at least 40% by weight of the water-immiscible carrier liquid.

10

Ethanol gives a cooling effect on application to skin, because it is very volatile. It is preferred that the content of ethanol or any monohydric alcohol with a vapour pressure above 1.3kPa (10mm Hg) is not over 15% better not  
15 over 8% by weight of the composition.

Fatty alcohols which are solid at room temperature, such as stearyl alcohol, lead to deposits with an opaque white appearance and are preferably kept to low concentration or  
20 excluded.

In a significant development of this invention, the sticks can be formulated to give a transparent or translucent appearance, which has two advantages. It assists with the  
25 avoidance of visible deposits on skin and also enables the

user to recognise, from the stick itself, that this will be the case.

We have found that compositions within this invention  
5 which are a novel transparent or translucent emulsion can be obtained by formulating the composition to meet two criteria. The first criterion is that the disperse phase and the continuous phase (consisting of the water-immiscible carrier liquid and the structurant contained within that liquid)  
10 should be formulated so that their refractive indices match. The refractive index of the continuous phase will be close to the refractive index of the water-immiscible carrier liquid in it. In order to achieve good light transmission through a composition, the refractive index of the water-immiscible  
15 continuous phase and the refractive index of the disperse phase should match within 0.003 units preferably 0.002 units.

The second criterion is that the matched refractive indices of these two phases should be an approximate match to  
20 the refractive index of the structurant. The closeness of match required will depend on the structurant which is used. The refractive index of a structurant can be determined by making trial compositions as explained in more detail below. Such investigation will also show how closely the refractive  
25 index of the liquid must be matched to the structurant.

A composition of this invention will generally be marketed in a container by means of which it can be applied at time of use. This container may be of conventional type.

5 A second aspect of the invention therefore provides an antiperspirant product comprising a dispensing container having at least one aperture for delivery of the contents of the container, means for urging the contents of the container to the said aperture or apertures, and a composition of the  
10 first aspect of the invention in the container. Preferred is that a composition of this invention is sufficiently rigid to be accommodated as a stick product in a dispensing container having an open end at which an end portion of the stick of composition is exposed for use.

15

The compositions of this invention can be produced by processes in which an emulsion is produced at an elevated temperature and allowed to cool to permit gel-formation in the continuous phase.

20

Thus, according to a third aspect of the present invention there is provided a process for the production of an antiperspirant composition according to the first aspect of this invention, comprising, not necessarily in any order,  
25 the steps of

- incorporating a structurant into a water-immiscible liquid carrier
  - mixing the liquid carrier with a disperse liquid phase which is a solution of an antiperspirant active in water, optionally mixed with a water-soluble solvent,
  - heating the liquid carrier or a mixture containing it to an elevated temperature at which the structurant is soluble in the water-immiscible liquid carrier,
- followed by
- introducing the mixture into a mould which preferably is a dispensing container, and then
  - cooling or permitting the mixture to cool to a temperature at which it is thickened or solidified.
- According to a fourth aspect of the present invention, there is provided a method for preventing or reducing perspiration on human skin comprising topically applying to the skin a composition according to the first aspect of this invention comprising an antiperspirant active, a water-immiscible liquid carrier and a structurant therefor.

#### DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

As indicated above, the composition contains an aqueous solution of antiperspirant active emulsified in a carrier oil



containing a structuring agent.

Materials which may be used to form these different parts of the composition will be discussed in turn, together  
5 with possibilities and preferences.

### Structurant

A number of organic compounds are known to possess the  
10 ability to gel hydrophobic organic liquids such as water-immiscible hydrocarbon and/or silicone oils by formation of a network of fibres or strands which extends throughout the liquid, thereby gelling the liquid. Such materials are generally non-polymeric, being monomers or dimers with  
15 molecular weight below 10,000 rather than polymers with more than 8 repeat units or with molecular weight above 10,000.

Materials with this property have been reviewed by Terech and Weiss in "Low Molecular Mass Gelators of Organic  
20 Liquids and the Properties of their Gels" Chem. Rev 97, 3133-3159 [1997] and by Terech in Chapter 8, "Low-molecular weight Organogelators" of the book "Specialist surfactants" edited by I D Robb, Blackie Academic Professional, 1997.

25 It is characteristic of such structurants, useful in

this invention, that

- they are able to gel the organic liquid in the absence of any disperse phase
- the structured liquids are obtainable by cooling from an elevated temperature at which the structurant is in solution in the liquid - this solution being mobile and pourable
- the structured liquid becomes more mobile if subjected to shear or stress
- the structure does not spontaneously recover within 24 hours if the sheared liquid is left to stand at ambient laboratory temperature, even though a small partial recovery may be observed
- the structure can be recovered by reheating to a temperature at which the structurant is in solution in the liquid and allowing it to cool back to ambient laboratory temperature.

It appears that such structurants operate by interactions which are permanent unless disrupted by shear or heating. Such structurants operate by forming a network of strands or fibres extending throughout the gelled liquid. In some cases these fibres can be observed by electron microscopy, although in other cases the observation of the fibres which are believed to be present is prevented by

practical difficulties in preparing a suitable specimen. When observed, the fibres in a gel are generally thin (diameter less than  $0.5\mu$ , often less than  $0.2\mu$ ) and appear to have numerous branches or interconnections.

5

If these fibres are crystalline, they may or may not be the same polymorph as macroscopic crystals obtained by conventional crystallization from a solvent.

10 One material which is well known to form such gels is 12-hydroxy stearic acid which is discussed in Terech et al "Organogels and Aerogels of Racemic and Chiral 12-hydroxy octadecanoic Acid", Langmuir Vol 10, 3406-3418, 1994. The material is commercially available from Ajinomoto and also  
15 from Caschem.

US-A-5750096 is one of several documents which teaches that gelation can be brought about using esters or amides of 12-hydroxy stearic acid. The alcohol used to form such an  
20 ester or the amine used to form such an amide may contain an aliphatic, cycloaliphatic or aromatic group with up to 22 carbons therein. If the group is aliphatic it preferably contains at least three carbon atoms. A cycloaliphatic group preferably contains at least five carbon atoms and may be a  
25 fixed ring system such as adamantyl.

N-acyl amino acid amides and esters are also known to structure liquids. We have established that they do so by forming fibrous networks. They are described in US patent 3969087. N-Lauroyl-L-glutamic acid di-n-butylamide is  
5 commercially available from Ajinomoto under their designation GP-1.

Further materials which have been disclosed as gelling agents are the amide derivatives of di and tribasic  
10 carboxylic acids set forth in WO 98/27954 notably alkyl N,N'dialkyl succinamides.

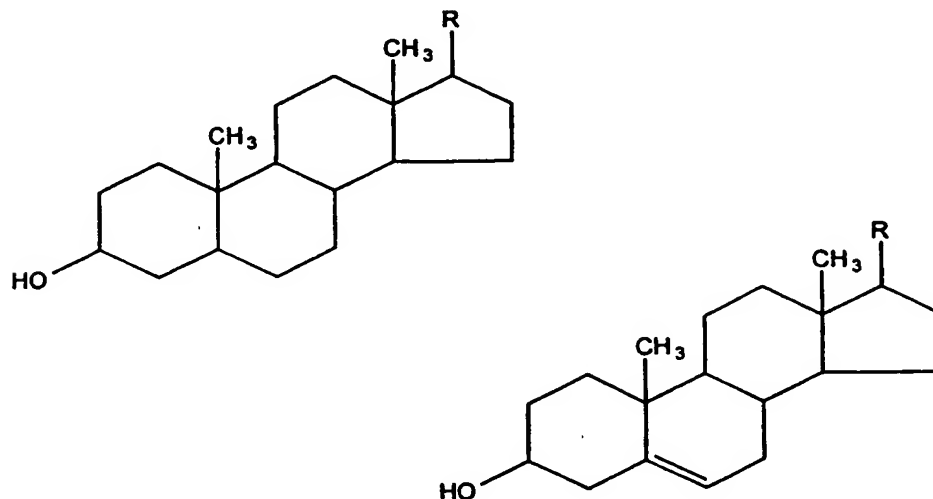
It is desirable that the structurant material(s) should not include carboxylic acid groups which can react with  
15 common antiperspirant acid salts in solution and form a precipitate of an insoluble aluminium or zirconium salt.

It is also desirable that the structurant material(s) should not include any functional groups which are vulnerable  
20 to hydrolysis under acidic aqueous conditions.

For these reasons the N-acylamino acid amides, the amides of 12-hydroxy stearic acid and the above-mentioned succinamides are of interest.

A novel structurant which is the subject of a co-pending application is a combination of a sterol and a sterol ester.

In its preferred form the sterol satisfies either of the  
5 two formulae:

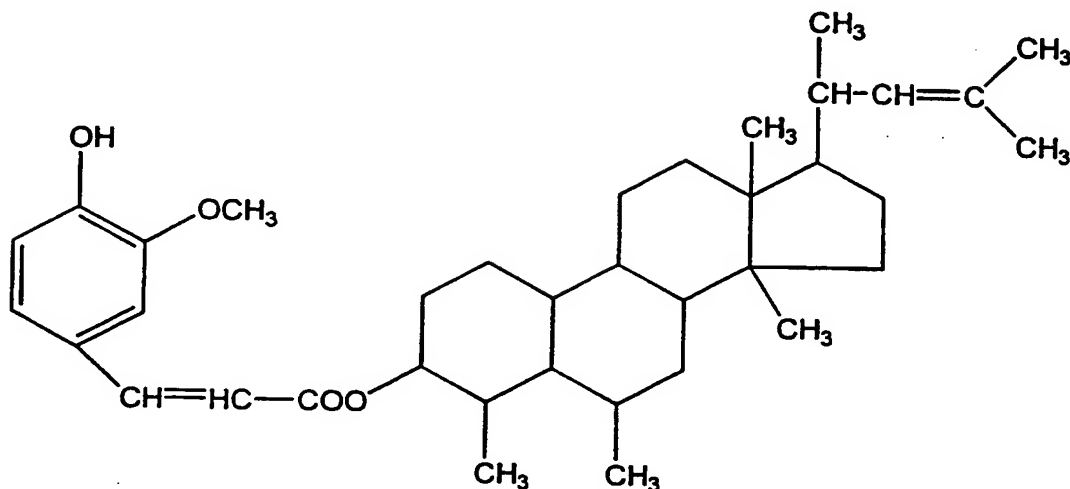


in which R represents an aliphatic, cycloaliphatic or aromatic group, and preferably a linear or branched aliphatic  
10 saturated or unsaturated hydrocarbon group. R desirably contains from 1 to 20 carbons and preferably from 4 to 14 carbons.

It is particularly suitable to employ  $\beta$  sitosterol or  
15 campesterol or cholesterol, or a hydrogenated derivative thereof, such as dihydrocholesterol, or a mixture of two or more of them. An especially preferred sterol is

$\beta$ -sitosterol.

The preferred sterol ester is oryzanol, sometimes referred to as  $\gamma$ -oryzanol which contains material satisfying the following formula:-

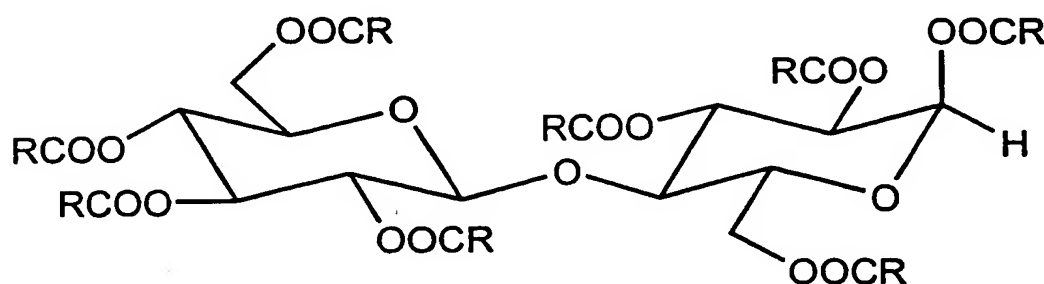


The sterol and sterol ester are used in a mole ratio that is normally selected in the range of from 10:1 to 1:10, especially from 6:1 to 1:4 and preferably in the range of from 3:1 to 1:2. Employment of the two system constituents within such a mole ratio range, and especially within the preferred range facilitates the co-stacking of the constituents and consequently facilitates the formation of a network that is readily able to structure the formulation.

Another novel structurant which is the subject of a co-pending application and which may be used in this invention is an ester of cellobiose and a fatty acid, preferably of 6

to 13 carbon atoms especially 8 to 10 or 11 carbon atoms. Preferably the cellobiose is fully esterified, or nearly so, and is in the  $\alpha$ -anomeric form.

- 5 The structure of such a compound, in its  $\alpha$ -anomeric form is:



where R is an alkyl or alkenyl chain of 5 to 12 carbon atoms so that the acyl group contains 6 to 13 carbon atoms.

- 10 Particularly preferred acyl groups incorporate a linear alkyl chain of 7 to 10 carbon atoms and are thus octanoyl, nonanoyl, decanoyl or undecanoyl.

The acyl groups may have a mixture of chain lengths but  
15 it is preferred that they are similar in size and structure. Thus it is preferred that all of the acyl groups are aliphatic and at least 90% of the acyl groups have a chain length within a range such that the shorter and longer chain lengths in the range differ by no more than two carbon atoms,

i.e. length in a range from  $m - 1$  to  $m + 1$  carbon atoms where the mean acyl chain length  $m$  has a value in a range from 7 to 10 or 11. Commercially available feedstocks for these acyl groups are likely to include a small percentage of acyl

5 groups which differ from the majority and may have a branched rather than linear chain. Thus it is likely that more than 90% but less than 100% of the acyl groups will meet the desired criterion of chain lengths in a range from  $m - 1$  to  $m + 1$  carbon atoms.

10

Linear aliphatic acyl groups may be obtained from natural sources, in which case the number of carbon atoms in the acyl group is likely to be an even number or may be derived synthetically from petroleum as the raw material in  
15 which case both odd and even numbered chain lengths are available.

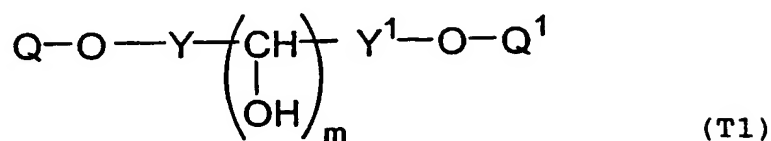
Synthetic methods for the esterification of saccharides are well known. The esterification of cellobiose has been  
20 reported by Takada et al in *Liquid Crystals*, (1995) Volume 19, pages 441-448. This article gives a procedure for the production of the alpha anomers of cellobiose octa-alkanoates by esterification of  $\beta$ -cellobiose using an alkanoic acid together with trifluoroacetic anhydride.

25



Further materials useful as structurants (and which are also the subject of a co-pending application) have the following general structure (T1):

5

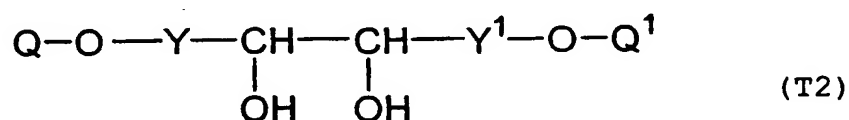


in which Y and Y<sup>1</sup> are independently -CH<sub>2</sub>- or >CO

10 Q and Q<sup>1</sup> are each a hydrocarbyl group of at least 6 carbon atoms and m is from 2 to 4, preferably 2.

It is preferred that m is 2 so that the structurant compounds comply with a general formula (T2):

15



The groups Y and Y<sup>1</sup> will usually be identical, i.e. both methylene or both carbonyl. The groups Q and Q<sup>1</sup> may not be the same but often will be identical to each other.

In the formula T2 above, if Y and Y<sup>1</sup> are methylene groups, the compound is a derivative of threitol, which is 25 1,2,3,4-tetrahydroxybutane, while if m is 2 and Y and Y<sup>1</sup> are

carbonyl groups, the compound is a diester of tartaric acid, which is 2,3-dihydroxybutane-1,4-dioic acid.

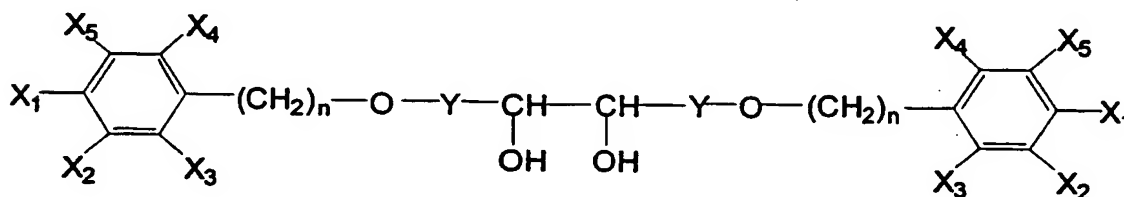
It is preferred that each group Q and Q<sup>1</sup> contains an aromatic nucleus which may be phenyl or, less preferably, some other aromatic group. Thus Q and Q<sup>1</sup> may be groups of the formula



where Ar denotes an aromatic nucleus, notably phenyl or substituted phenyl and n is from 0 to 10.

An aromatic nucleus (Ar) is preferably unsubstituted or substituted with one or more substituents selected from alkyl, alkyloxy, hydroxy, halogen or nitro.

One substituent may be an alkyl or alkyloxy group with a long alkyl chain. Thus a formula for preferred forms of these structurants can be given as



where

n = 0 to 10, preferably 0 to 3, more preferably 1, 2 or 3;

$Y = -CH_2-$  or  $>C=O$

$X_1 = H, Cl, Br, F, OH, NO_2, O-R,$  or  $R,$  where  $R$  is an aliphatic hydrocarbon chain with 1 to 18 carbon atoms.

$X_2$  to  $X_5$  are each independently  $H, Cl, Br, F, OH, NO_2, OCH_3,$   
5 or  $CH_3$

In these formulae above, the central carbon atoms which bear hydroxy groups are chiral centres. Thus if  $m = 2,$   $Y$  and  $Y^1$  are the same and  $Q$  and  $Q^1$  are the same, the compounds will  
10 exist as  $R,R$  and  $S,S$  optically active forms as well as an optically inactive  $R,S$  form. We may prefer to use the optically active  $R,R$  or  $S,S$  forms or a mixture of the two - which may be a racemic mixture.

15 Compounds within the general formulae T1 and T2 are available commercially. Also, syntheses of these compounds have been given in scientific literature where the compounds were being used as intermediates for purposes not related to the present invention. Thus syntheses of threitol  
20 derivatives can be found in:

Kataky et al, J. Chem Soc Perkin Trans vol 2 page 321 [1990]

Tamoto et al, Tetrahedron Vol 40 page 4617 [1984], and

Curtis et al, J.C.S. Perkin I Vol 15 page 1756 [1977].

Preparations of tartrate esters are found at:

25 Hu et al J. Am. Chem. Soc. Vol 118, 4550 [1996] and

Bishop et al J. Org Chem Vol56 5079 [1991].

The amount of structurant in an emulsion composition of this invention is likely to be up to 25% or 30% by weight of the continuous phase, more likely from 1% or 2% up to 16% or 20% of this phase. In examples below, amounts of 4.8% and above, not exceeding 16%, are commonly used. As a percentage of the whole composition the amount is from 1% up to 20%, probably from 1 to 12% or 15%.

10

If a structurant is a combination of two materials, or if two structurants are used together, then the above percentages apply to the total amount of structurant.

#### 15 Carrier liquid

The water-immiscible carrier liquid in the continuous phase comprises one or a mixture of materials which are relatively hydrophobic so as to be immiscible in water. Some hydrophilic liquid may be included in the carrier, provided the overall carrier liquid mixture is immiscible with water. It will generally be desired that this carrier is liquid (in the absence of structurant) at temperatures of 15°C and above. It may have some volatility but its vapour pressure will generally be less than 4 kPa (30 mm Hg) at 25°C so that the

material can be referred to as an oil or mixture of oils.  
More specifically, it is desirable that at least 80% by  
weight of the hydrophobic carrier liquid should consist of  
materials with a vapour pressure not over this value of 4 kPa  
5 at 25°C.

It is preferred that the hydrophobic carrier material  
includes a volatile liquid silicone, i.e. liquid  
polyorganosiloxane. To class as "volatile" such material  
10 should have a measurable vapour pressure at 20 or 25°C.  
Typically the vapour pressure of a volatile silicone lies in  
a range from 1 or 10 Pa up to 2 kPa at 25°C.

It is desirable to include volatile silicone because it  
15 gives a "drier" feel to the applied film after the  
composition is applied to skin.

Volatile polyorganosiloxanes can be linear or cyclic or  
mixtures thereof. Preferred cyclic siloxanes include  
20 polydimethylsiloxanes and particularly those containing from 3  
to 9 silicon atoms and preferably not more than 7 silicon  
atoms and most preferably from 4 to 6 silicon atoms,  
otherwise often referred to as cyclomethicones. Preferred  
linear siloxanes include polydimethylsiloxanes containing  
25 from 3 to 9 silicon atoms. The volatile siloxanes normally

by themselves exhibit viscosities of below  $10^{-5}$  m<sup>2</sup>/sec (10 centistokes), and particularly above  $10^{-7}$  m<sup>2</sup>/sec (0.1 centistokes), the linear siloxanes normally exhibiting a viscosity of below  $5 \times 10^{-6}$  m<sup>2</sup>/sec (5 centistokes). The

5 volatile silicones can also comprise branched linear or cyclic siloxanes such as the aforementioned linear or cyclic siloxanes substituted by one or more pendant  $-O-Si(CH_3)_3$  groups. Examples of commercially available silicone oils include oils having grade designations 344, 345, 244, 245 and

10 246 from Dow Corning Corporation; Silicone 7207 and Silicone 7158 from Union Carbide Corporation; and SF1202 from General Electric.

The hydrophobic carrier employed in compositions herein

15 can alternatively or additionally comprise non-volatile silicone oils, which include polyalkyl siloxanes, polyalkylaryl siloxanes and polyethersiloxane copolymers. These can suitably be selected from dimethicone and dimethicone copolyols. Commercially available non-volatile

20 silicone oils include Dow Corning 556 and Dow Corning 200 series.

The water-immiscible liquid carrier may contain from 0 to 100% by weight of one or more liquid silicones.

25 Preferably, there is sufficient liquid silicone to provide at

least 10%, better at least 15%, by weight of the whole composition. If silicone oil is used, volatile silicone preferably lies in a range from 20% possibly from 30 or 40% up to 100% of the weight of the water-immiscible carrier liquid. In many instances, when a non-volatile silicone oil is present, its weight ratio to volatile silicone oil is chosen in the range of from 1:3 to 1:40.

Silicon-free hydrophobic liquids can be used instead of, or more preferably in addition to liquid silicones. Silicon-free hydrophobic organic liquids which can be incorporated include liquid aliphatic hydrocarbons such as mineral oils or hydrogenated polyisobutene, often selected to exhibit a low viscosity. Further examples of liquid hydrocarbons are polydecene and paraffins and isoparaffins of at least 10 carbon atoms.

Other hydrophobic carriers are liquid aliphatic or aromatic esters. Suitable aliphatic esters contain at least one long chain alkyl group, such as esters derived from  $C_1$  to  $C_{20}$  alkanols esterified with a  $C_8$  to  $C_{22}$  alkanolic acid or  $C_6$  to  $C_{10}$  alkanedioic acid. The alkanol and acid moieties or mixtures thereof are preferably selected such that they each have a melting point of below  $20^\circ\text{C}$ . These esters include isopropyl myristate, lauryl myristate, isopropyl palmitate,

diisopropyl sebacate and diisopropyl adipate.

Suitable liquid aromatic esters, preferably having a melting point of below 20°C, include fatty alkyl benzoates.

- 5 Examples of such esters include suitable C<sub>8</sub> to C<sub>18</sub> alkyl benzoates or mixtures thereof.

Further instances of suitable hydrophobic carriers comprise liquid aliphatic ethers derived from at least one  
10 fatty alcohol, such as myristyl ether derivatives e.g. PPG-3 myristyl ether or lower alkyl ethers of polyglycols such as PPG-14 butyl ether.

Aliphatic alcohols which are solid at 20°C, such as  
15 stearyl alcohol are preferably absent or present in low concentration such as less than 5% by weight of the whole composition since these lead to visible white deposits when a composition is used.

20 However, aliphatic alcohols which are liquid at 20°C may be employed. These include branched chain alcohols of at least 10 carbon atoms such as isostearyl alcohol and octyl dodecanol.

25 Very polar materials are preferably excluded or present



in only small quantity in the water-immiscible carrier liquid. Preferably therefore, this liquid or mixture of liquids contains not more than 10% of its own weight, better not more than 5%, of any constituent which is a water-  
5 miscible compound.

Silicon-free liquids can constitute from 0-100% of the water-immiscible liquid carrier, but it is preferred that silicone oil is present and that the amount of silicon-free  
10 constituents preferably constitutes up to 50 or 60% and in many instances from 10 or 15% up to 50 or 60% by weight of the carrier liquid.

If any oxygen-containing silicon-free organic liquids  
15 are included in the hydrophobic carrier liquid, the amount of them is likely to be not over 70% by weight of the carrier liquid. Smaller amounts, ranging up to 20, 30 or 35% by weight are likely.

20 The carrier liquid must be compatible with the structurant. If the structurant is too soluble or conversely is very insoluble in the carrier liquid it may fail to form a gel and the carrier liquid should be modified to alter its polarity.

Disperse Phase Solvent

The disperse phase is a solution of an antiperspirant active ingredient in a solvent which is more polar than the carrier liquid of the disperse phase. This disperse phase comprises water as solvent and can comprise one or more water-soluble or water-miscible liquids in addition to water.

One class of water soluble or water-miscible liquids comprises short chain monohydric alcohols, e.g. C<sub>1</sub> to C<sub>4</sub> and especially ethanol or isopropanol, which can impart a deodorising capability to the formulation. A further class of hydrophilic liquids comprises diols or polyols preferably having a melting point of below 40°C, or which are water miscible. Examples of water-soluble or water-miscible liquids with at least one free hydroxy group include ethylene glycol, 1,2-propylene glycol, 1,3-butylene glycol, hexylene glycol, diethylene glycol, dipropylene glycol, 2-ethoxyethanol, diethylene glycol monomethylether, triethyleneglycol monomethylether and sorbitol. Especially preferred are propylene glycol and glycerol.

The disperse phase constitutes from 25 to 85% of the weight of the composition preferably from 25 to 80% more

preferably from 25 or 35% up to 50 or 65%, while the continuous phase with the structurant therein provides the balance from 15 or 35% up to 75% of the weight of the composition. Compositions with a high proportion of  
5 disperse phase i.e. from 65 to 85% disperse phase may be advantageous because the large proportion of disperse phase can make a contribution to hardness. The proportion of water in an emulsion according to the present invention is often selected in the range of up to 60%, and particularly  
10 from 10% up to 40% or 50% of the whole formulation.

A composition of this invention will generally include one or more emulsifying surfactants which may be anionic, cationic, zwitterionic and/or nonionic surfactants. The  
15 proportion of emulsifier in the composition is often selected in the range up to 10% by weight and in many instances from 0.1 or 0.25 up to 5% by weight of the composition. Most preferred is an amount from 0.1 or 0.25 up to 3% by weight. Nonionic emulsifiers are frequently  
20 classified by HLB value. It is desirable to use an emulsifier or a mixture of emulsifiers with an overall HLB value in a range from 2 to 10 preferably from 3 to 8.

It may be convenient to use a combination of two or  
25 more emulsifiers which have different HLB values above and

below the desired value. By employing the two emulsifiers together in appropriate ratio, it is readily feasible to attain a weighted average HLB value that promotes the formation of an emulsion.

5

Many suitable emulsifiers of high HLB are nonionic ester or ether emulsifiers comprising a polyoxyalkylene moiety, especially a polyoxyethylene moiety, often containing from about 2 to 80, and especially 5 to 60  
10 oxyethylene units, and/or contain a polyhydroxy compound such as glycerol or sorbitol or other alditol as hydrophilic moiety. The hydrophilic moiety can contain polyoxypropylene. The emulsifiers additionally contain a hydrophobic alkyl, alkenyl or aralkyl moiety, normally  
15 containing from about 8 to 50 carbons and particularly from 10 to 30 carbons. The hydrophobic moiety can be either linear or branched and is often saturated, though it can be unsaturated, and is optionally fluorinated. The hydrophobic moiety can comprise a mixture of chain lengths, for example  
20 those deriving from tallow, lard, palm oil, sunflower seed oil or soya bean oil. Such nonionic surfactants can also be derived from a polyhydroxy compound such as glycerol or sorbitol or other alditols. Examples of emulsifiers include cetareth-10 to -25, ceteth-10-25, steareth-10-25 (i.e. C<sub>16</sub>  
25 to C<sub>18</sub> alcohols ethoxylated with 10 to 25 ethylene oxide

residues) and PEG-15-25 stearate or distearate. Other suitable examples include C<sub>10</sub>-C<sub>20</sub> fatty acid mono, di or tri-glycerides. Further examples include C<sub>18</sub>-C<sub>22</sub> fatty alcohol ethers of polyethylene oxides (8 to 12 EO).

5

Examples of emulsifiers, which typically have a low HLB value, often a value from 2 to 6 are fatty acid mono or possibly diesters of polyhydric alcohols such as glycerol, sorbitol, erythritol or trimethylolpropane. The fatty acyl moiety is often from C<sub>14</sub> to C<sub>22</sub> and is saturated in many instances, including cetyl, stearyl, arachidyl and behenyl. Examples include monoglycerides of palmitic or stearic acid, sorbitol mono or diesters of myristic, palmitic or stearic acid, and trimethylolpropane monoesters of stearic acid.

15

A particularly desirable class of emulsifiers comprises dimethicone copolymers, namely polyoxyalkylene modified dimethylpolysiloxanes. The polyoxyalkylene group is often a polyoxyethylene (POE) or polyoxypropylene (POP) or a copolymer of POE and POP. The copolymers often terminate in C<sub>1</sub> to C<sub>12</sub> alkyl groups.

Suitable emulsifiers and co-emulsifiers are widely available under many trade names including Abil™, Arlacel™, Brij™, Cremophor™, Dehydrol™, Dehymuls™, Emerest™,

25

Lameform™, Pluronic™, Prisorine™, Quest PGPR™, Span ™, Tween ™, SF1228, DC3225C and Q2-5200.

### Antiperspirant Actives

5

Antiperspirant actives, are preferably incorporated in an amount of from 0.5-60%, particularly from 5 to 30% or 40% and especially from 5 or 10% to 30 or 35% of the weight of the whole composition.

10

Antiperspirant actives for use herein are often selected from astringent active salts, including in particular aluminium, zirconium and mixed aluminium/zirconium salts, including both inorganic salts, salts with organic anions and complexes. Preferred astringent salts include aluminium, zirconium and aluminium/zirconium halides and halohydrate salts, such as chlorohydrates.

20

Aluminium halohydrates are usually defined by the general formula  $Al_2(OH)_xQ_y \cdot wH_2O$  in which Q represents chlorine, bromine or iodine, x is variable from 2 to 5 and  $x + y = 6$  while  $wH_2O$  represents a variable amount of hydration. Especially effective aluminium halohydrate salts, known as activated aluminium chlorohydrates, are described in EP-A-

25

6739 (Unilever NV et al), the contents of which  
specification is incorporated herein by reference. Some  
activated salts do not retain their enhanced activity in the  
presence of water but are useful in substantially anhydrous  
5 formulations, i.e. formulations which do not contain a  
distinct aqueous phase.

Zirconium actives can usually be represented by the  
empirical general formula:  $ZrO(OH)_{2n-nz}B_z \cdot wH_2O$  in which  $z$  is a  
10 variable in the range of from 0.9 to 2.0 so that the value  
 $2n-nz$  is zero or positive,  $n$  is the valency of  $B$ , and  $B$  is  
selected from the group consisting of chloride, other  
halide, sulphamate, sulphate and mixtures thereof. Possible  
hydration to a variable extent is represented by  $wH_2O$ .  
15 Preferable is that  $B$  represents chloride and the variable  $z$   
lies in the range from 1.5 to 1.87. In practice, such  
zirconium salts are usually not employed by themselves, but  
as a component of a combined aluminium and zirconium-based  
antiperspirant.

20

The above aluminium and zirconium salts may have  
coordinated and/or bound water in various quantities and/or  
may be present as polymeric species, mixtures or complexes.  
In particular, zirconium hydroxy salts often represent a  
25 range of salts having various amounts of the hydroxy group.

Zirconium aluminium chlorohydrate may be particularly preferred.

Antiperspirant complexes based on the above-mentioned  
5 astringent aluminium and/or zirconium salts can be employed. The complex often employs a compound with a carboxylate group, and advantageously this is an amino acid. Examples of suitable amino acids include dl-tryptophan, dl- $\beta$ -phenylalanine, dl-valine, dl-methionine and  $\beta$ -alanine, and  
10 preferably glycine which has the formula  $\text{CH}_2(\text{NH}_2)\text{COOH}$ .

It is highly desirable to employ complexes of a combination of aluminium halohydrates and zirconium chlorohydrates together with amino acids such as glycine,  
15 which are disclosed in US-A-3792068 (Luedders et al). Certain of those Al/Zr complexes are commonly called ZAG in the literature. ZAG actives generally contain aluminium, zirconium and chloride with an Al/Zr ratio in a range from 2 to 10, especially 2 to 6, an Al/Cl ratio from 2.1 to 0.9 and  
20 a variable amount of glycine. Actives of this preferred type are available from Westwood, from Summit and from Reheis.

Other actives which may be utilised include astringent  
25 titanium salts, for example those described in GB 2299506A.



The proportion of solid antiperspirant salt in the composition normally includes the weight of any water of hydration and any complexing agent that may also be present in the solid active. However, when the active salt is in solution, its weight excludes any water present.

The antiperspirant active will often provide from 3 to 60% by weight of the aqueous disperse phase, particularly from 10% or 20% up to 55% or 60% of that phase.

10

#### Optional ingredients

Optional ingredients in compositions of this invention can include deodorants, for example at a concentration of up to about 10% w/w. Suitable deodorant actives can comprise deodorant effective concentrations of antiperspirant metal salts, deoperfumes, and/or microbicides, including particularly bactericides, such as chlorinated aromatics, including biguanide derivatives, of which materials known as Irgasan DP300 <sup>™</sup> (Triclosan), Tricloban <sup>™</sup>, and Chlorhexidine warrant specific mention. A yet another class comprises biguanide salts such as available under the trade mark Cosmosil <sup>™</sup>.

Other optional ingredients include wash-off agents,

often present in an amount of up to 10% w/w to assist in the removal of the formulation from skin or clothing. Such wash-off agents are typically nonionic surfactants such as esters or ethers containing a C<sub>8</sub> to C<sub>22</sub> alkyl moiety and a hydrophilic moiety which can comprise a polyoxyalkylene group (POE or POP) and/or a polyol.

Another optional constituent of the formulation is a polymeric secondary structurant. Examples of such structurants which can be employed include polymeric waxes and organo polysiloxane elastomers such as reaction products of a vinyl terminated polysiloxane and a cross linking agent or alkyl or alkyl polyoxyalkylene-terminated poly (methyl substituted) or poly (phenyl substituted) siloxanes.

Polymers containing both siloxane and hydrogen bonding groups, which might be used as secondary structurants, have been disclosed in WO 97/36572 and WO 99/06473. A number of polyamides have also been disclosed as structurants for hydrophobic liquids. Polyacrylamides, polyacrylates or polyalkylene oxides may be used to structure or thicken the disperse phase if it is aqueous.

The compositions herein can incorporate one or more cosmetic adjuncts conventionally contemplatable for antiperspirant solids or soft solids. Such cosmetic

adjuncts can include skin feel improvers, such as talc or finely divided polyethylene, for example in an amount of up to about 10%; skin benefit agents such as allantoin or lipids, for example in an amount of up to 5%; colours; skin cooling agents other than the already mentioned alcohols, such a menthol and menthol derivatives, often in an amount of up to 2%, all of these percentages being by weight of the composition. A commonly employed adjunct is a perfume, which is normally present at a concentration of from 0 to 4% and in many formulations from 0.25 to 2% by weight of the composition.

#### Translucent/Transparent Compositions

A composition of this invention can be formulated such that the emulsion is translucent or transparent. In order to do this the refractive indices of the water-immiscible continuous phase and the polar or aqueous disperse phase must be matched to each other and the value of refractive index at which they are matched must also approximately match the refractive index of the structurant.

The refractive index of a fibrous network of a structurant can be determined by using that structurant to gel a number of oils or oil mixtures of differing refractive

index. When the resulting gel is transparent, the refractive index of the oil or oil mixture (which can be determined by conventional measurement) is a good approximation to the refractive index of the structurant.

- 5 The oils or mixtures or oils should be chosen from these which are gelled well by the structurant to avoid interfering effects. When the gel is not transparent, but is translucent, it will indicate a refractive index which is not precisely matched to the refractive index of the
- 10 structurant, and thus indicate an amount of mismatch which can be tolerated without loss of translucency. It is likely that the matched refractive indices of the liquid phases will be not over 0.07 units below and not over 0.04 units above the refractive index of the structurant.

15

Some examples of oils which may be used to make mixtures which vary in refractive index are:

- volatile silicone (refractive index of about 1.40)
- 20 • C<sub>12-15</sub> alkyl benzoate (refractive index of about 1.48) which available as Finsolv TN and/or
- octylmethoxycinnamate (refractive index of about 1.54) which is available as Parsol MCX.
- polyphenylsiloxane (DC70) (refractive index of about
- 25 1.53)

Using this method we have determined the refractive indices of some structurants, namely:-

	N-lauroyl L-glutamic acid di-n-butylamide	approx 1.48
5	12-hydroxy stearic acid	approx 1.52
	$\alpha$ -cellobiose octa-esters with C <sub>8</sub> to C <sub>12</sub>	
	fatty acids	approx 1.48

For the continuous phase, silicon-free water-immiscible  
10 liquid oils generally have refractive indices in a range  
from 1.43 to 1.49 at 22°C and can be used alone or mixed  
together to give a silicon-free carrier liquid with  
refractive index in this range. Volatile silicone oils  
generally have a refractive index slightly below 1.40 at  
15 22°C, but carrier liquid mixtures with refractive indices in  
the range from 1.41 to 1.46 can be obtained by mixing  
volatile silicone with other oils. Non-volatile silicone  
oils generally have refractive indices in a range from 1.45  
to 1.48 at 22°C and so can be included when desired.

20

The refractive index of the continuous phase will be  
very close to the refractive index of the carrier liquid  
(usually a carrier liquid mixture) which is its principal  
component.

25

For the disperse phase, a solution of an antiperspirant active salt in water alone will generally display a refractive index below 1.425. The refractive index can be raised by incorporating a diol or polyol into the aqueous solution. It is believed to be novel to match the refractive index of a polar disperse phase to that of a structurant network within a continuous phase. Moreover, it can be achieved without using so much diol or polyol as will make the composition excessively sticky.

10

For the regular production of compositions with optimum transparency it may prove desirable to monitor the refractive indices of the raw materials to detect any batch to batch variation. If necessary the composition of a liquid phase can be adjusted by variation of the quantity of a constituent material.

15

### Mechanical Properties and Product Packages

20

The compositions of this invention are structured liquids and may be firm or soft in appearance. Even a soft solid has an ability to sustain its own shape, for instance if it is removed from a mould without being subjected to shear it will retain its shape for at least 30 seconds,

25

usually longer, at about 20°C.

A composition of this invention will usually be marketed as a product comprising a container with a quantity  
5 of the composition therein, where the container has at least one aperture for the delivery of composition, and means for urging the composition in the container towards the delivery aperture. Conventional containers take the form of a barrel of oval cross section with the delivery aperture(s) at one  
10 end of the barrel.

A composition of this invention is preferably sufficiently rigid that it is not apparently deformable by hand pressure, even though a surface layer will transfer as  
15 a film to skin, and is suitable for use as a stick product in which a quantity of the composition in the form of a stick is accommodated within a container barrel having an open end at which an end portion of the stick of composition is exposed for use. The opposite end of the barrel is  
20 closed.

Generally the container will include a cap for its open end and a component part which is sometimes referred to as an elevator or piston fitting within the barrel and capable  
25 of relative axial movement along it. The stick of

46

composition is accommodated in the barrel between the piston and the open end of the barrel. The piston is used to urge the stick of composition along the barrel. The piston and stick of composition may be moved axially along the barrel  
5 by manual pressure on the underside of the piston using a finger or rod inserted within the barrel. Another possibility is that a rod attached to the piston projects through a slot or slots in the barrel and is used to move the piston and stick. Preferably the container also  
10 includes a transport mechanism for moving the piston comprising a threaded rod which extends axially into the stick through a correspondingly threaded aperture in the piston, and means mounted on the barrel for rotating the rod. Conveniently the rod is rotated by means of a  
15 handwheel mounted on the barrel at its closed end, i.e. the opposite end to the delivery opening.

If a composition of this invention is softer, but still capable of sustaining its own shape it will be more suited  
20 for dispensing from a barrel with a closure instead of an open end, where the closure has one or more apertures through which composition from the barrel can be extruded. The number and design of such apertures is at the discretion of the designer of the package.

25



The component parts of such containers are often made from thermoplastic materials, for example polypropylene or polyethylene. Descriptions of suitable containers, some of which include further features, are found in US patents  
5 4865231, 5000356 and 5573341.

### Measurement of Properties

#### i) Penetrometer

The hardness and rigidity of a composition which is a  
10 firm solid can be determined by penetrometry. If the composition is a softer solid, this will be observed as a substantial lack of any resistance to the penetrometer probe.

15 A suitable procedure is to utilise a lab plant PNT penetrometer equipped with a Seta wax needle (weight 2.5 grams) which has a cone angle at the point of the needle specified to be  $9^{\circ}10' \pm 15'$ . A sample of the composition with a flat upper surface is used. The needle is lowered  
20 onto the surface of the composition and then a penetration hardness measurement is conducted by allowing the needle with its holder to drop under a total weight, (i.e. the combined weight of needle and holder) of 50 grams for a period of five seconds after which the depth of penetration  
25 is noted.

Desirably the test is carried out at a number of points on each sample and the results are averaged. Utilising a test of this nature, an appropriate hardness for use in an open-ended dispensing container is a penetration of less  
5 than 30 mm in this test, for example in a range from 2 to 30 mm. Preferably the penetration is in a range from 5mm to 20 mm.

In a specific protocol for this test measurements on a  
10 stick were performed in the stick barrel. The stick was wound up to project from the open end of the barrel, and then cut off to leave a flat, uniform surface. The needle was carefully lowered to the stick surface, and then a penetration hardness measurement was conducted. This  
15 process was carried out at six different points on the stick surface. The hardness reading quoted is the average value of the 6 measurements.

ii) Texture analyser

20 The hardness of a softer solid can be measured by using a texture analyser. This test apparatus can move a blunt probe into or out from a sample at a controlled speed and at the same time measure the applied force. The parameter which is determined as hardness is a function of the peak  
25 force and the projected area of indentation.

A specific test protocol used a Stable Micro systems TA.XT2i Texture Analyser. A metal sphere, of diameter 9.5mm, was attached to the underside of the *Texture Analyser's* 5 kg load cell such that it could be used for indenting a sample placed beneath it on the base plate of the instrument. After positioning the sample, the sphere position was adjusted until it was just above the sample surface. *Texture Expert Exceed* software was used to generate the subsequent motion profile used in the test method. This profile initially indented the sphere into the sample at an indentation speed of 0.05mm/s until a designated force was reached, which was chosen such that the distance of penetration into the sample was less than the radius of the sphere. At this load the direction of motion of the sphere was immediately reversed to withdraw the sphere from the sample at the same speed of 0.05mm/s. During the course of the test, the data acquired were time(s), distance (mm) and force (N) and the data acquisition rate was 25 Hz.

20

Suitable samples for measurement were either contained in stick barrels, which had a screw mechanism, or in 15 ml glass jars. For the barrel samples, the stick was wound up until it protruded above the edges of the barrel and then a knife was used to skim the top of the barrel in such a way

as to leave a flat uniform surface. The stick was then pushed back into the barrel as far as possible to minimise any mechanical interference resulting from the compliance of the screw mechanism in the pack. Two indents were generally made either side of the screw. The samples in the 15 ml jars needed no surface preparation but only had enough surface area for a single indentation test to be performed.

The data associated with each test were manipulated using standard spreadsheet software and used to calculate the hardness,  $H$ , using the following equation:

$$H[N/mm^2] = \frac{F_{\max}[N]}{A_p[mm^2]}$$

where  $F_{\max}$  is the peak load and  $A_p$  is the projected area of the indentation remaining on unloading. This area can be calculated geometrically from the plastic indentation depth. This is slightly less than the total penetration depth measured under load because of elastic deformation of the sample. The plastic indentation depth is calculated from a graph of the unloading-force-versus-total-penetration-depth. The initial slope of this unloading data depends on the initial elastic recovery of the sample. The plastic indentation depth is estimated from an intercept between the

zero force axis and a straight line drawn at a tangent to the initial part of the unloading slope.

Similar hardness measurements were also done using a  
5 desktop *Instron Universal Testing Machine* (Model 5566)  
fitted with a 10 N load cell, and the data analysis  
performed in the same way.

iii) Deposition and whiteness of deposit

10 Another test of the properties of a composition is the  
amount of the composition which is delivered onto a surface  
when the composition is drawn across that surface  
(representing the application of a stick product to human  
skin). To carry out this test of deposition, a sample of  
15 the composition with standardised shape and size is fitted  
to apparatus which draws the sample across a test surface  
under standardised conditions. The amount transferred to  
the surface is determined as an increase in the weight of  
the substrate to which it is applied. If desired the  
20 colour, opacity or clarity of the deposit may subsequently  
be determined.

A specific procedure for such tests used apparatus to  
apply a deposit from a stick onto a substrate under  
25 standardised conditions and then measures the mean level of

white deposits using image analysis.

The substrates used were

- a: 12 x 28cm strip of grey abrasive paper (3M™ P800  
5 WetorDry™ Carborundum paper)
- b: 12 x 28cm strip of black Worsted wool fabric.

The substrates were weighed before use. The sticks  
were previously unused and with domed top surface unaltered.

10

The apparatus comprised a flat base to which a flat  
substrate was attached by a clip at each end. A pillar  
having a mounting to receive a standard size stick barrel  
15 was mounted on an arm that was moveable horizontally across  
the substrate by means of a pneumatic piston.

Each stick was kept at ambient laboratory temperature  
overnight before the measurement was made. The stick was  
20 advanced to project a measured amount from the barrel. The  
barrel was then placed in the apparatus and a spring was  
positioned to biased the stick against the substrate with a  
standardised force. The apparatus was operated to pass the  
stick laterally across the substrate eight times. The  
25 substrate was carefully removed from the rig and reweighed.

Whiteness of Deposit

The deposits from the previous test were assessed for  
5 their whiteness after an interval of 24 hours approximately.

This was done using a Sony XC77 monochrome video camera  
with a Cosmocar 16mm focal length lens positioned vertically  
above a black table illuminated from a high angle using  
10 fluorescent tubes to remove shadowing. The apparatus was  
initially calibrated using a reference grey card, after the  
fluorescent tubes had been turned on for long enough to give  
a steady light output. A cloth or Carborundum paper with a  
deposit thereon from the previous test was placed on the  
15 table and the camera was used to capture an image. An area  
of the image of the deposit was selected and analysed using  
a Kontron IBAS image analyser. This notionally divided the  
image into a large array of pixels and measured the grey  
level of each pixel on a scale of 0 (black) to 255 (white).  
20 The average of the grey intensity was calculated. This was  
a measure of the whiteness of the deposit, with higher  
numbers indicating a whiter deposit. It was assumed that  
low numbers show a clear deposit allowing the substrate  
colour to be seen.

It has been found desirable to carry out deposition of a standard stick composition in the manner specified above, and determine the whiteness of the deposit, as a control.

5 iv) Light transmission

The translucency of a composition may be measured by placing a sample of standardised thickness in the light path of a spectrophotometer and measuring transmittance, as a percentage of light transmitted in the absence of the gel.

10

We have carried out this test using a dual-beam spectrophotometer. The sample of composition was poured hot into a 4.5 ml cuvette made of polymethylmethacrylate (PMMA) and allowed to cool to an ambient temperature of 20-25°C.

15 Such a cuvette gives a 1 cm thickness of composition.

Measurement was carried out at 580 nm, with an identical but empty cuvette in the reference beam of the spectrophotometer, after the sample in the cuvette had been held for 24 hours. We have observed that a composition

20 which gives a transmittance of as little as 1% in this test is perceived by eye as "translucent". If a stick is made from a composition with 3% transmittance, it is possible to see cavities made by boring beneath the surface of the sample. By contrast, a conventional stick structure with  
25 stearyl alcohol is so opaque that it is impossible to see



beneath its surface. A transmittance measured at any temperature in the range from 20-25°C is usually adequately accurate, but measurement is made at 22°C if more precision is required. In a number of preferred examples we have  
5 achieved a transmittance of 20% or above.

### Preparation

Compositions of this invention can be produced by  
10 processes which involve forming a heated mixture of the composition at a temperature such that the structurant is in solution in the continuous phase, pouring that mixture into a mould, which may take the form of a dispensing container, and then cooling the mixture whereupon the structurant  
15 solidifies within water-immiscible liquid phase, and thereby gels that phase and hence the whole composition.

A convenient process sequence comprises first forming a solution of the structurant in the water-immiscible liquid.  
20 This is normally carried out by agitating the mixture at a temperature sufficiently high that all the structurant dissolves (the dissolution temperature) such as a temperature in a range from 50 to 120°C.

25 If any emulsifier is being used, this is conveniently

mixed into this liquid phase. Separately an aqueous or hydrophilic disperse phase is prepared by introduction of antiperspirant active into the liquid part of that phase (if this is necessary; antiperspirant actives can sometime be  
5 supplied in aqueous solution which can be utilised as is). This solution of antiperspirant active which will become the disperse phase is preferably heated to a temperature similar to that of the continuous phase with structurant therein, but without exceeding the boiling point of the solution and  
10 then mixed with the continuous phase. Alternatively the solution is introduced at a rate which maintains the temperature of the mixture. If necessary a pressurised apparatus could be used to allow a higher temperature to be reached. After the two phases are mixed, the resulting  
15 mixture is introduced into a dispensing container such as a stick barrel. This is usually carried out at a temperature 5 to 30°C above the setting temperature of the composition. The container and contents are then cooled to ambient temperature. Cooling may be brought about by nothing more  
20 than allowing the container and contents to cool. Cooling may be assisted by blowing ambient or even refrigerated air over the containers and their contents.

**EXAMPLES**

The examples below were prepared using a number of materials set out with their proprietary names in the following list. All temperature are in degrees Celsius. Refractive indices were measured at 22°C.

- 1 & 2) Volatile cyclic silicones (cyclomethicones)  
DC 245 and DC 345 (Dow Corning)
- 10 3 & 4) Non-volatile silicone fluids  
DC 556 and DC 710 (Dow Corning)
- 5) Polydecene (Silkflo 364NF from Albemarle)
- 6) Isostearyl Alcohol (abbreviated to ISA -  
Prisorine 3515 from Unichema)
- 15 7) C12-15 alkyl benzoate (Finsolv TN from Fintex)
- 8) Mineral Oil (Sirius M70 from Dalton)
- 9) Polypropyleneglycol 14 butylether (Fluid AP from  
Amercol)
- 10) Isopropyl myristate (abbreviated to IPM from  
20 Unichema)
- 11) Isohexadecane (Permethyl 101A from Presperse Inc)
- 12) Isoeicosane (Permethyl 102A from Presperse Inc)
- 13) Cetyl dimethicone copolyol (Abil EM90 emulsifier  
from Th. Goldschmidt)
- 25 14) C20-C40 alcohols (Unilin 425 from Petrolite)
- 15) 50% aqueous solution of Al/Zr pentachlorohydrate  
(Zirkonal 50 from Giulini)
- 16) Al/Zr Tetrachlorohydrex glycine complex 30% in  
propylene glycol (WA2Z 8106 from Westwood)
- 30 17) Al/Zr tetrachlorohydrex glycine complex (AZG 375  
from Summit)

- 18) Glycerol (from Aldrich)
- 19) Propylene glycol (from Fisons)
- 20) N-lauryl-L-glutamic acid di-n-butylamide (GP1 from Ajinomoto)
- 5 21)  $\beta$ -sitosterol (available as ultrasitosterol from Kaukas)
- 22)  $\beta$ -sitosterol (from Acros Organics)
- 23)  $\gamma$ -oryzanol (from Jan Dekker (UK) Ltd)
- 24) Dihydrocholesterol (from Acros Organics)
- 10 25) (R,R) -1,4-Di-O-Benzyl-D-Threitol (Sigma Aldrich)
- 26) (R,R) -1,4-chlorobenzyl-D-Threitol (Sigma Aldrich)
- 27) Bis-phenylpropyldimethicone, a non-volatile silicone fluid (SF 1555 from G E Silicones)
- 28) Polyglyceryl polyricinolate (Quest PGPR)
- 15 29) 1-octyldodecanol (Eutanol G from Henkel/Cognis)
- 30) Hydrogenated polyisobutene (Panalene-L-14E from Amoco)
- 31) Hydrogenated polyisobutene (Fancol 800 from Fanning Corporation)
- 20 32) Polyglyceryl-3-diisostearate (Lameform TGI from Henkel/Cognis)
- 33) Polyglyceryl-2-dipolyhydroxystearate (Dehymuls PGPH from Henkel/Cognis)
- 34) Polyalpha Olefins (Puresyn 4 from Mobil Chemical)
- 25 35) Cetareth 20 (Eumulgin B2 from Henkel)

Example 1

Emulsion sticks were prepared with formulations as set out in the table below.

5

To prepare these sticks, the cyclomethicone was mixed with the other organic liquids including the cetyl dimethicone copolyol which functioned as an emulsifier (silicone surfactant) and with the GP1 structurant. The mixture was heated with gentle stirring to a temperature of 120°C to dissolve the structurant. It was then allowed to cool to 100°C.

The disperse phase (also referred to as internal phase) was an aluminium zirconium active dissolved in a polyol and water. This disperse phase was pre-heated to 92°C and added slowly to the organic liquids over a period of one minute while mixing with a Silverson mixer. After addition was complete the formulation was mixed at higher speed for five minutes. Stirring speed was then reduced for a further one minute after which the mixture was poured into stick barrels and allowed to cool undisturbed to ambient laboratory temperature. The sticks were tested by penetrometer, in one case by texture analyser, and for whiteness of deposits by the test procedures given earlier.

25

It was observed that the sticks were translucent.

Examples		1.1	1.2	1.3	1.4
		Parts by weight			
5	Cyclomethicone DC 245 (1)	18	22.25	21.7	-
	Cyclomethicone DC 345 (2)	-	-	-	23.7
	Mineral Oil (8)	-	-	-	-
10	Polydecene (5)	22.75	27.5	27.4	-
	Finsolv TN (7)	13.3	13.3	13.3	12.6
	Isostearyl alcohol (6)	12	12	12	11.5
	GP-1 (20)	4	4	4	3.8
15	Cetyl Dimethicone Copolyol (13)	1	1	1	0.95
	Zirconal 50 (15)	40	40	40	40
	Glycerol (18)	-	-	-	10
		Properties			
	penetration depth (mm)	18.7	21.6	17.0	17.5
20	Hardness by texture analyser (N/mm <sup>2</sup> )	-	-	-	0.067
	Whiteness on grey paper 24 hours after deposition	26	-	-	32
25	Whiteness on black wool 24 hours after deposition				19

**Example 2**

Sticks were prepared with formulations tabulated below. As the first step, the hydrophobic phase was prepared by combining the cosmetic oils and solvents, the emulsifier  
5 introduced and dissolved in a Silverson mixer. The oryzanol (the sterol ester) was introduced and dissolved by heating and stirring 500 rpm. Once the oryzanol had dissolved completely, the sterol was added and the mixture again heated and stirred until a clear solution had been obtained.  
10 The solution was then allowed to cool under gentle stirring until it reached a temperature of about 5-10 degrees above its gelling point determined in a preliminary trial.

In a second step, the aqueous phase was prepared by  
15 combining the antiperspirant solution with the other aqueous phase components. This was heated to the same temperature as the continuous phase solution.

In the third step, the aqueous phase was introduced slowly  
20 into the hydrophobic phase whilst mixing with the Silverson mixer and maintained at a constant temperature and at constant shear conditions. The mixture was sheared for up to 10 minutes, until the aqueous phase had been evenly dispersed. The resulting emulsion was left to stand and to de-aerate. It  
25 was then poured into stick barrels and allowed to cool to laboratory ambient temperature and solidify. A number of the

resultant sticks were evaluated for penetration, deposition and whiteness by the methods described above after the stick had been maintained for at least 24 hours at ambient laboratory temperature.

5	<b>Example</b>	<b>2.1</b>	<b>2.2</b>	<b>2.3</b>	<b>2.4</b>	<b>2.5</b>	<b>2.6</b>	<b>2.7</b>	<b>2.8</b>	<b>2.9</b>
		<b>Weight % in formulation</b>								
	<b>Continuous phase</b>									
	Cyclomethicone DC 345 (2)	23.5	32.4	40.0	35.0	30.0	40.0	40.0	40.0	35.0
10	PPG-14 Butylether (9)	-	5.0	-	-	-	-	-	-	-
	C <sub>12-15</sub> Alkyl Benzoate (7)	12.5	12.7	10.0	-	20.0	-	-	-	-
	Isostearyl Alcohol (6)	-	-	-	-	-	10.0	10.0	-	-
	Polydecene (5)	11.3	-	-	-	-	-	-	-	-
15	Isopropyl Myristate (10)	-	-	-	15	-	-	-	10.0	15.0
	Beta Sitosterol (21)	2.4	2.5	-	-	-	2.5	-	2.5	2.5
	Beta Sitosterol (22)	-	-	2.5	2.5	2.5	-	-	-	-
	Dihydrocholesterol (24)	-	-	-	-	-	-	2.5	-	-
	Oryzanol (23)	2.4	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
20	Cetyl Dimethicone Copolyol (13)	0.9	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	<b>Aqueous Phase</b>									
	Zirkonal 50 (15)	37.6	39.9	40.0	40.0	40.0	40.0	40.0	40.0	40.0
	Glycerol (18)	9.4	4.0	4.0	4.0	-	-	-	4.0	4.0
25	Water	-	-	-	-	4.0	4.0	4.0	-	-
	Penetrometer hardness (mm)	16.9	17.8	17.1			22.4	26.7		18.8
30	Whiteness on grey paper 24 hours after deposition	22	28	26				22		
	Whiteness on black wool 24 hours after deposition	15	11	14				29		
35										



Example	2.10	2.11	2.12	2.13	2.14	2.15	2.16	2.17	CWS
	Weight % in formulation								
<b>Continuous phase</b>									
5 Cyclomethicone DC 345 (2)	35.0	35.0	35.0	35.0	25.0	35.0	34.0	33.0	
C <sub>12-15</sub> Alkyl Benzoate (7)	7.5	-	15.0	7.5	25.0	-	7.5	7.5	
Isostearyl Alcohol (6)	-	-	-	-	-	-	7.5	7.5	
10 Polydecene (5)	-	-	-	-	-	-	-	-	
Isopropyl Myristate (10)	7.5	15.0	-	7.5	-	15.0	-	-	
Beta Sitosterol (22)	2.5	2.5	2.5	2.5	2.5	2.5	3.0	3.5	
Oryzanol (23)	2.5	2.5	2.5	2.5	2.5	2.5	3.0	3.5	
15 Cetyl Dimethicone Copolyol (13)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
<b>Aqueous Phase</b>									
Zirkonal 50 (15)	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0	
Glycerol (18)	4.0	-	-	-	-	-	-	-	
20 Water	-	4.0	4.0	4.0	4.0	4.0	4.0	4.0	
Penetrometer hardness (mm)	17.0	20.7	27.4	18.2	18.5	17.6	15.6	12.5	9.4
25 Whiteness on grey paper 24 hours after deposition		29	30	31			26	25	118
Whiteness on black wool 24 hours after deposition		12	12	8			12	12	186

30 All of the compositions in this Example gave slightly translucent or opaque medium hard to hard white sticks. Qualitative assessment showed that all gave lower white deposits on skin than a conventional white solid stick (cws) structured with 15% stearyl alcohol and 3% castor wax,

included as the last column of the table above.

### Example 3

Cellobiose was esterified with nonanoic acid to yield the  
5 fully esterified product in the form of its  $\alpha$ -anomer following  
a procedure generally as described in Takada et al, Liquid  
Crystals, Volume 19, page 441 (1995).

The following materials were used:

- 10  $\beta$ -D-cellobiose, 20 grams, 0.058 moles  
Nonanoic acid, 591.6 grams, 3.74 moles  
Trifluoroacetic anhydride, 297.6 grams, 1.42 moles.

These materials were obtained from Acros Organics -  
15 Fisher Scientific.

Into a 2 litre flange pot equipped with an overhead  
stirrer, water condenser and addition inlet was placed the  
nonanoic acid together with the trifluoroacetic anhydride.  
20 The resultant clear mixture was stirred up and heated to 100°C  
using a silicone oil bath and temperature probe. During  
heating it was noted that the colour of the reaction mixture  
darkened and developed a dark brown tinge. After allowing the  
mixture to stir for one hour at 100°C, the cellobiose was  
25 slowly added via a solid powder funnel to the dark activated  
solution, and a dirty brown suspension was formed which re-

dissolved forming a clear black solution within 10-20 minutes.

The reaction flask was then maintained at 100°C for a total of 6 hours then cooled down to ambient laboratory  
5 temperature. Next the contents of the flask were transferred into 2 litres of methanol containing 10% de-ionised water in an ice-cooled 5 litre beaker. Immediately an off-white solid precipitate came out of solution, this was filtered off and collected. The crude solid was recrystallised a total of 4  
10 times from a tetrahydrofuran/methanol solution producing a white solid product.

The product cellobiose octa-nonanoate also designated esterified cellobiose - C<sub>9</sub> was obtained in a quantity of 31.5  
15 g which was a 37% yield. It had a melting point of 110°C. The infra-red spectrum showed an absorption peak at 1739 cm<sup>-1</sup> for the ester carbonyl group. The amount of free acid could be determined from its absorption peak at 1705 cm<sup>-1</sup>.

20 The n.m.r. spectrum showed the amount of cellobiose which was fully esterified to be 93.5% and showed the proportions of product which were the  $\alpha$ - and  $\beta$ -anomers, (93.5%  $\alpha$ -anomer).

This procedural route was also used to prepare the  
25 corresponding ester of cellobiose and decanoic acid.

Opaque emulsion sticks were prepared with these cellobiose esters as structurant in formulations as set out in tables below.

5        To prepare these sticks, the cyclomethicone was mixed with the other organic liquids (if any) including the cetyl dimethicone copolyol which functioned as an emulsifier (silicone surfactant) and the mixture was heated with gentle stirring to a temperature 5 to 10°C above the temperature at  
10 which the structurant had been found to dissolve. The esterified cellobiose was then added and allowed to dissolve.

The disperse phase (also referred to as internal phase) was an aluminium zirconium active dissolved in water or in a  
15 mixture of a polyol and water. This disperse phase was pre-heated to the same temperature as the organic oils containing the esterified cellobiose and added slowly to them over a period of one minute while mixing with a Silverson mixer. After addition was complete the formulation was mixed at  
20 higher speed for five minutes. Stirring speed was then reduced for a further one minute after which the mixture was poured into stick barrels and allowed to cool undisturbed to ambient laboratory temperature. The sticks were tested by penetrometer, by texture analyser and for whiteness of  
25 deposits, in each instance by the test procedures given earlier. All of the sticks were opaque although without the

chalky white appearance of a commercial white stick structured with stearyl alcohol and castor wax.

<b>Examples</b>		<b>3.1</b>	<b>3.2</b>	<b>3.3</b>	<b>3.4</b>	<b>3.5</b>	<b>3.6</b>
5		<b>% by weight</b>					
	Cyclomethicone DC 245 (1)	18	22.25	21.7	45.5	-	-
	Cyclomethicone DC 345 (2)	-	-	-	-	23.8	24.4
10	Mineral Oil (8)	-	-	-	-	22.9	23.4
	Polydecene (5)	22.75	27.5	27.4	-	-	-
	PPG-14 Butyl Ether (9)	4.5	5.5	5.4	-	-	-
15	Cellobiose octa-nonanoate	3.75	3.75	4.5	-	-	-
	Cellobiose octa-decanoate	-	-	-	2.5	4.8	2.4
	Cetyl Dimethicone Copolyol (13)	1	1	1	2	1	1
20	Zirconal 50 (15)	40	40	40	40	38	38
	Glycerol (18)	-	-	-	-	9.5	10.8
	Water	10			10	-	-
		<b>Properties</b>					
25	penetration depth (mm)	16.8	17.5	15.7	40	12.5	-
	Hardness by texture analyser (N/mm <sup>2</sup> )	0.11	0.10	0.12	-	-	-
30	Whiteness on grey paper 24 hours after deposition	19	16	16	31	-	-
	Whiteness on black wool 24 hours after deposition	28	29	27	11	-	-

68

Examples		3.7	3.8	3.9	3.10	3.11	3.12
		% by weight					
5	Cyclomethicone DC 245 (1)	-	23.5	20.95	19.8	20.95	22.3
	Cyclomethicone DC 345 (2)	23.3	-	-	-	-	-
	Mineral Oil (8)	23.3	22.2				21.0
	Polydecene (5)				25.9		
	PPG-14 Butyl Ether (9)				-		
10	DC 556 (3)			24.75			
	Isostearyl alcohol (6)	-	-	-	-	24.8	-
	Cellobiose octa-nonanoate	-	-	-	-	-	-
15	Cellobiose octa-decanoate	2.4	2.5	2.5	2.5	2.5	5
	Cetyl Dimethicone Copolyol (13)	1	1.8	1.8	1.8	1.75	1.7
	Zirkonal 50 (15)	40	40	40	40	40	40
20	Glycerol (18)	10	10	10	10	10	10
	Water	-	-	-	-	-	-
		Properties					
25	penetration depth (mm)		22.7	25.6	25.0	29.0	17.8
	Hardness by texture analyser (N/mm <sup>2</sup> )						
30	Whiteness on grey paper 24 hours after deposition		27	25	22	23	28
	Whiteness on black wool 24 hours after deposition		17	13	15	11	16

35

**Example 4**

The procedure used in Example 3 was repeated to prepare a number of emulsion sticks with formulations set out in the following tables. The continuous and disperse phases were formulated to have refractive indices which matched closely at the value given in the tables. These sticks were tested as before and their properties are also given in these tables.

70

Examples		4.1	4.2	4.3	4.4	4.5	4.6
		% by weight					
5	Cyclomethicone DC245 (1)	22.625	18.75	25.5	19	26	17.75
	Mineral Oil (8)	22.625	-	-	-	-	-
	Polydecene (5)	-	22.5	15.75	22	15	22
10	PPG-14 Butyl Ether (9)	-	4	4	-	-	4.25
	Isostearyl Alcohol (6)	-	-	-	4.25	4.25	-
	Cellobiose octa-nanoate	3.75	3.75	3.75	3.75	3.75	5
15	Cetyl Dimethicone Copolyol (13)	1	1	1	1	1	1
	Zirkonal 50 (15)	40	40	40	40	40	40
	Glycerol (18)	10	10	7.5	10	7.5	10
	Water	-	-	2.5	-	2.5	-
		Properties					
20	Matched refractive index of phases	1.43	1.43	1.425	1.435	1.425	1.43
	penetration depth (mm)	19.3	18.5	17.3	24.7	23.6	12.4
25	Hardness by texture analyser (N/mm <sup>2</sup> )	0.11	0.12	0.08	0.07	0.06	0.17
	Whiteness on grey paper 24 hours after deposition	-	15	16	18	19	16
30	Whiteness on black wool 24 hours after deposition	-	24	28	25	30	26
	Transmittance at 580nm	-	38%	33%	41%	35%	51%

35



Examples		4.7	4.8	4.9	4.10	4.11	4.12
		% by weight					
5	Cyclomethicone DC245 (1)	16.75	18	14.02	28.4	4.5	-
	Cyclomethicone DC345 (2)	-	-	-	-	-	4.4
	Mineral Oil (8)	-	-	-	-		43.4
	Polydecene (5)	20.75	22.75	17.72	13.1	50.75	-
	PPG-14 Butyl Ether (9)	4	4.5	3.51	3.75	-	-
10	Isostearyl Alcohol (6)	-	-	-	-	-	-
	Cellobiose octa-nanoate	7.5	3.75	3.75	3.75	3.75	-
	Cellobiose octa-decanoate	-	-	-	-	-	2.4
15	Cetyl Dimethicone Copolyol (13)	1	1	1	1	1	1
	Zirkonal 50 (15)	40	-	40	40	-	
	Westwood Active (16)	-	-	-	-	-	48.8
20	Glycerol (18)	10	4	17.5	6.25	12	-
	Water	-	14	2.5	3.75	8	-
	Propylene glycol (19)	-	12	-	-	-	-
	AZG 375 (17)	-	20	-	-	20	-
		Properties					
25	Matched refractive index of phases	1.43	1.43	1.43	1.42	1.45	1.46
	penetration depth (mm)	11	14.5	14.9	15.1	14.8	-
	Hardness by texture analyser (N/mm <sup>2</sup> )	0.29	0.11	0.14	0.13	0.11	-
30	Whiteness on grey paper 24 hours after deposition	17	20	18	21	16	-
	Whiteness on black wool 24 hours after deposition	25	28	25	31	19	-
35	Transmittance at 580nm	48%	82%	65%	30%	72%	74%

<b>Examples</b>		<b>4.13</b>	<b>4.14</b>	<b>4.15</b>	<b>4.16</b>	<b>4.17</b>
		<b>% by weight</b>				
5	Cyclomethicone DC245 (1)	41.85	35.4	10.04	10.64	6.96
	Permethyl 101A (11)	2.15	-	-	-	-
	Permethyl 102A (12)	-	8.6	-	-	-
	Polydecene (5)	-	-	12.7	13.45	8.8
	PPG-14 Butyl Ether (9)	-	-	2.51	2.66	1.74
10	Isostearyl Alcohol (6)	-	-	-	-	-
	Cellobiose octa-nonanoate	5	5	3.75	2.25	1.5
	Cetyl Dimethicone Copolyol (13)	1	1	1	1	1
	Zirkonal 50 (15)	40	40	52.71	52.71	60.24
15	Glycerol (18)	0.75	4.5	17.29	17.29	19.76
	Water	9.25	5.5	-	-	-
		<b>Properties</b>				
20	Matched refractive index of phases	1.40	1.41	1.43	1.43	
	penetration depth (mm)	13.5	13.2	12.0	16.8	
	Hardness by texture analyser (N/mm <sup>2</sup> )	0.16	0.15	0.13	0.07	
25	Whiteness on grey paper 24 hours after deposition	59	61	24	24	
	Whiteness on black wool 24 hours after deposition	122	24	15	16	
30	Transmittance at 580nm	2.7%	5%	33%	73%	

Example 5

Opaque emulsion sticks were prepared with formulations as set out in the tables below.

5

To prepare these sticks, the structurant compound was mixed with the carrier liquid including the cetyl dimethicone copolyol which functioned as an emulsifier (silicone surfactant) and the mixture was heated with gentle stirring  
10 until the structurant dissolved. The temperature was then adjusted to about 90°C.

The disperse phase (also referred to as internal phase) was an aluminium zirconium active dissolved in water and  
15 slightly diluted with additional water. This disperse phase was pre-heated to about 90°C, i.e. the same temperature as the organic liquid mixture containing the structurant and added slowly to them over a period of one minute while mixing with a Silverson mixer. After addition was complete the formulation  
20 was mixed at higher speed for five minutes. After this the mixture was poured into stick barrels and allowed to cool undisturbed to ambient laboratory temperature. The sticks were tested by penetrometer, by texture analyser and for whiteness of deposits, in each instance by the test procedures  
25 given earlier. All of the sticks were opaque.

Examples	5.1	5.2
	% by weight	
(R,R)-1,4-Di-O-Benzyl-D-Threitol	-	7%
5 (R,R)-1,4-Bis-O-(4-Chlorobenzyl)-D-Threitol	5%	-
DC 345 (2)	35%	33.4%
Finsolv TN (7)	9%	8.6%
Abil EM 90 (13)	1%	1%
10 Zirkonal 50 (15)	40%	40%
Water	10%	10%
	Properties	
Hardness N/mm <sup>2</sup>	0.09	0.11
15 Whiteness on grey paper 24 hours after deposition	n/d	34
Whiteness on black wool 24 hours after deposition	n/d	13

These stick were found to have a gentle, silky feel when  
 20 applied to skin.

Example 6

12-hydroxystearic acid was converted to the corresponding amide by reaction with 1,1'-carbonyldiimidazole. The  
5 procedure was as follows:

To a three necked 1 litre round bottom flask equipped with water condenser, overhead mechanical stirrer and pressure equalising funnel was added 12-hydroxystearic acid (15.0g,  $4.75 \times 10^{-2}$  mol) followed by 300 mls of tetrahydrofuran. To  
10 this was then added 1,1'-carbonyldiimidazole (8.9g,  $5.50 \times 10^{-2}$  mol) and the reaction left stirring at 40°C for 1 hour, after which time ammonia gas was bubbled through for a period of 2 hours, the reaction being kept at 40°C. After this time the reaction was cooled to room temperature and the  
15 tetrahydrofuran removed in vacuo. The solid white was then washed successively with 4 x 200 mls of water and then filtered. The white compound was then dried in a vacuum oven and recrystallised from ethanol to give a white solid.

20 The product, 12-hydroxystearamide, was obtained in 60% yield. It had melting point 98-99°C and its structure was confirmed by proton n.m.r. and infra red spectroscopy. Peaks were observed at  $1654\text{cm}^{-1}$  and  $3209\text{cm}^{-1}$ .

25 The material was used as a structurant in translucent sticks of the formulation shown in the table below, which also

76

includes properties of the sticks as determined by test procedures described earlier. The preparation of sticks was by the same method used in Example 5. The gelation temperature was noted as about 85°C.

5

10

15

20

Ingredient		% by weight
12-hydroxystearamide		6%
GP-1 (20)		2%
DC 245 (1)		40%
Finsolv TN (7)		10%
Abil EM 90 (13)		1%
Zirkonal 50 (15)		41%
Properties		
Penetrometer Hardness (mm)		17.8
Whiteness on grey sandpaper 24 hours after deposition		24
Whiteness on black wool 24 hours after deposition		26

**Example 7**

Sticks were prepared using the procedure given in Example 3. The sticks were tested for hardness by texture analyser and/or by penetrometer. They were observed to give deposits of low whiteness, but numerical data were not recorded.

For some sticks in this example the refractive indices of the water-immiscible continuous phase and the polar antiperspirant active solution were matched sufficiently to give translucent sticks. Some values of transmittance are shown.

Examples	7.1	7.2	7.3	7.4	7.5
	% by weight				
DC245 (1)	44	21.625	21.625	21.625	18
Silkflo364 (5)	-	-	-	21.625	4
Permethyl 102A (12)	--	21.625	-	-	-
SF1555 (27)	-	-	21.625	-	22
Abil EM90 (13)	1	-	-	-	1
Quest PGPR (28)	-	1.75	1.75	1.75	-
Esterified Cellobiose -C9	5	5	5	5	5
Zirkonal 50 (15)	39	40	40	40	40
Glycerol (18)	-	8	9	8.75	10
Water	11	2	1	1.25	-
	Properties				
Penetration depth (mm)	9.3	12	11.3	13	
Hardness by texture analyser (N/mm <sup>2</sup> )	0.1	0.12	0.12	0.21	0.13

Examples		7.6	7.7	7.8	7.9	7.10
		% by weight				
5	Cyclomethicone DC 245 (1)	7	6.8	36.5	1.7	1.25
	isostearyl alcohol (6)	-	-	-	23.3	-
	octyldodecanol (29)	-	-	-	-	23.1
	SF1555 (27)	34.5	37.7	7	-	-
	Silkflo 364 (5)	-	-	-	16.8	17.65
10	Esterified Cellobiose -C10	7.5	7.3	7.8	7	7
	Cetyl Dimethicone Copolyol (Abil EM90) (13)	1	1	1	1	1
	Zirconal 50 (15)	-	-	-	-	-
15	Westwood active (16)	40	41	42	40	40
	Glycerol (18)	-	4.7	5.2	6.8	6.5
	Water	10	1.5	0.5	3.4	3.5
		Properties				
20	Matched refractive index of phases	1.45	1.45	1.46	1.45	1.45
	penetration depth (mm)	9.1	6.9	8.7	8.8	9.1
	Hardness by texture analyser (N/mm <sup>2</sup> )	0.37	0.03	0.08	0.04	0.19
	Transmittance at 580nm (%)	8	3	5	6	5



Examples	7.11	7.12	7.13	7.14
	% by weight			
DC245 (1)	12	11.32	-	-
Silkflo 364 (5)	32.5	30.68	39	41.5
Abil EM90 (13)	0.5	0.5	1	1
Esterified Cellobiose -C10	5	7.5	10	7.5
Zirkonal 50 (15)	33	33	-	-
Westwood active (16)	-	-	50	50
Glycerol (18)	17	17	-	-
	Properties			
penetration depth (mm)	19	14	7.3	9.6
Hardness by texture analyser (N/mm <sup>2</sup> )	0.44	0.07	0.47	0.15

**Example 8**

The procedure used in Example 3 was repeated to prepare a number of emulsion sticks with formulations set out in the following tables. As in Example 4, the continuous and disperse phases were formulated to have refractive indices which matched closely at the value given in the tables. The sticks were tested for hardness by texture analyser and/or by penetrometer. They were observed to give deposits of low whiteness, consistent with their good transparency, but numerical data were not recorded.

The refractive indices of sample quantities of the water-immiscible liquid mixture and the antiperspirant active solutions were checked before making the sticks. If necessary their formulations were modified very slightly to optimise the refractive index match.

Examples	8.1	8.2	8.3	8.4	8.5	8.6
	% by weight					
Permethyl 102A (12)	41.36	-	-	-	-	-
Panalene L-14E (30)	-	-	22	-	-	-
Fancol 800 (31)	-	-	-	22	22	-
Puresyn 4 (34)	-	-	-	-	-	22
DC245 (1)	2.64	11.4	22	22	22	22
SF 1555 (27)	-	34.1	-	-	-	-
Esterified cellobiose C9	5	4.9	5	5	5	5
Abil EM90 (13)	1	1	1	1	1	1
Zirkonal 50 (15)	-	-	40	40	36.6	40
Westwood active (16)	50	48.6	-	-	-	-
Glycerol (18)	-	-	9.35	7.5	13.4	8.75
Water	-	-	0.65	2.5	-	1.25
	Properties					
Matched RI of phases (at 25°C)	1.46	1.45	1.431	1.425	1.437	1.429
penetration depth (mm)	9	11	10.5	12.1	7.9	8.8
Hardness by texture analyser (N/mm <sup>2</sup> )	0.11	0.11	0.13	0.12±	0.11	0.104
Transmittance at 580nm (%)	68	70	40	6.4	70	37

Examples	8.7	8.8	8.9	8.10	8.11
	% by weight				
DC245 (1)	22	22.25	22.25	21.625	-
DC556 (3)	22	-	-	-	-
Silkflo364 (5)	-	-	-	-	44
Permethyl 102A (12)	-	22.25	-	-	-
Panalene-L-14E (30)	-	-	-	21.625	-
SF1555 (27)	-	-	22.25	-	-
Abil EM90 (13)	1	0.5	0.5	-	1
Lameform TGI (32)	-	-	-	0.875	-
Dehymuls PGPH (33)	-	-	-	0.875	-
Esterified cellobiose C9	5	5	5	5	5
Zirkonal 50 (15)	40	40	40	40	50
Glycerol (18)	9	8	9	9.8	-
Water	1	2	1	0.2	
	Properties				
Matched RI of phases (at 25°C)	1.428	1.43	1.43	1.43	1.46
penetration depth (mm)	9.0	11	11	10.5	9
Hardness by texture analyser (N/mm <sup>2</sup> )	0.10	0.09	0.16	0.13	0.13
Transmittance at 580nm (%)	40	22	33	36	24

	Examples	8.12	8.13	8.14	8.15	8.16	8.17
		% by weight					
5	DC245 (1)	-	-	-	22	22	18
	Silkflo364 (5)	44	-	-	-	-	5.3
	Permethyl 102A (12)	-	44	-	22	-	-
	Panalene-L-14E (30)	-	-	44	-	-	-
	SF1555 (27)	-	-	-	-	22	-
10	Octyldodecanol (29)	-	-	-	-	-	21.9
	Abil EM90 (13)	1	1	1	1	1	1
	Esterified cellobiose C9	5	5	5	5	5	5
	Zirkonal 50 (15)	18	21.5	12	-	-	37.8
	AZG-375 (17)	-	-	-	25	25	-
15	Glycerol (18)	32	28.5	38	0.6	2.5	11
	Water	-	-	-	24.4	22.5	-
		Properties					
20	Matched refractive index of phases (at 25°C)	1.45	1.45	1.46	1.43	1.43	1.43
	penetration depth (mm)	9	9	7	9	8	-
	Hardness by texture analyser (N/mm <sup>2</sup> )	0.13	0.15	0.20	-	0.21	0.12
25	Transmittance at 580nm (%)	74	46	82	53	41	24

**Example 9**

The procedure for making sticks used in Example 3 was used to prepare translucent emulsion sticks with the formulation below in which the structurant is  $\alpha$ -cellobiose octa-undecatoate ("CB11"). As in Example 4, the continuous and disperse phases were formulated to have refractive indices which matched closely at the value given. The sticks were tested for hardness by texture analyser and/or by penetrometer. They were observed to give deposits of low whiteness.

Ingredients	percent by weight
DC245 (1)	11
Silkflo 364 (5)	33
Abil EM90 (13)	1
Esterified cellobiose C11 "CB-11"	5
Zirkonal 50 (15)	33
Glycerol (18)	17
Properties	
Matched RI of phases (at 25°C)	1.44
penetration depth (mm)	16
Hardness by texture analyser (N/mm <sup>2</sup> )	0.05
Transmittance at 580nm (%)	6

**Example 10**

The procedure used in Example 3 was used to prepare an opaque emulsion stick of the following formulation, which  
5 included agents to assist wash-off.

	Ingredients	percent by weight
	DC245 (1)	16.4
	Silkflo 364 (5)	24.6
	Abil EM90 (13)	1
10	Esterified cellobiose C9	5
	Zirkonal 50 (15)	40
	Glycerol (18)	10
	Ceteareth 20 (35)	2.5
15	C <sub>20-40</sub> alcohols (14)	0.5

CLAIMS

1. An antiperspirant composition which is a structured emulsion comprising
  - i) 15 to 75% by weight of a continuous phase containing  
5 water-immiscible liquid carrier and at least one gel-forming structurant therein,
  - ii) 25 to 85% by weight of a disperse phase which is a solution of antiperspirant active in water, optionally including water-soluble solvent,
- 10 wherein said at least one structurant has a molecular weight of less than 10000, provides a network of fibres in the liquid carrier and is present in an amount which is from 1% to 20% by weight of the antiperspirant composition.
- 15 2. A composition according to claim 1 wherein the structurant is present in an amount from 1 to 15% of the composition.
3. A composition according to claim 1 or claim 2 wherein  
20 the continuous phase with structurant therein is a gel which is able to melt to become mobile on heating.
4. A composition according to any one of the preceding claims wherein the continuous phase contains liquid silicone  
25 in an amount which is at least 10% by weight of the whole

composition.

5. A composition according to any one of the preceding claims wherein the continuous phase contains hydrocarbon oil  
5 in an amount which is at least 10% by weight of the liquid carrier.
6. A composition according to any one of the preceding claims wherein the continuous phase does not contain more  
10 than 10% of its own weight, better not more than 5%, of any constituent which is a water-miscible compound.
7. A composition according to any one of the preceding claims wherein the continuous phase is from 35 to 75% of the  
15 weight of the composition and the disperse phase is from 25 to 65% of the weight of the composition.
8. A composition according to any one of the preceding claims wherein the continuous phase is from 15 to 60% of the  
20 weight of the composition and the disperse phase is from 40 to 85% of the weight of the composition.
9. A composition according to any one of the preceding claims wherein the total amount of structurant is from 0.5 to  
25 25% by weight of the continuous phase.



10. A composition according to any one of the preceding claims wherein the total amount of structurant is from 1% to 12% by weight of the whole composition.

5 11. A composition according to any one of the preceding claims wherein the disperse phase contains a diol or polyol with a solubility in water of at least 10% by weight at 22°C.

12. A composition according to any one of the preceding  
10 claims wherein the composition contains an antiperspirant active selected from the group of antiperspirant compounds of aluminium, zirconium and mixtures thereof in an amount from 5 to 35% by weight of the composition.

15 13. A composition according to claim 12 characterised in that the antiperspirant active comprises an aluminium and/or zirconium halohydrate, an activated aluminium and/or zirconium halohydrate, or an aluminium and/or zirconium complex or an activated aluminium and/or zirconium complex.

20

14. A composition according to claim 13 which is a halohydrate of complex in which aluminium and zirconium are both present.

25 15. A composition according to any one of the preceding

claims which contains from 0.1% to 10% by weight of a nonionic emulsifier.

16. A composition according to any one of the preceding  
5 claims which is a firm gel such that a penetrometer needle with a cone angle of 9 degrees 10 minutes, drops into the gel for no more than 30 mm when allowed to drop under a total weight of 50 grams for 5 seconds.
- 10 17. A composition according to any one of the preceding claims which is translucent or transparent.
18. A composition according to claim 17 which has at least 1%, preferably at least 3% light transmittance at 580 nm  
15 through a 1cm thickness of the composition at 22°C.
19. A composition according to claim 17 which has at least 20% light transmittance at 580 nm through a 1cm thickness of the composition at 22°C.
- 20
20. A composition according to any one of claims 1 to 19, accommodated within a dispensing container.
21. An antiperspirant product comprising a composition  
25 according to any one of claims 1 to 19 and a dispensing

container with the composition therein, said container having at least one aperture for delivery of the contents of the container and means for urging the contents of the container to the said aperture or apertures.

5

22. A product according to claim 21 wherein the composition is in the form of a stick and the container has an open end at which an end portion of the stick of composition is exposed for use.

10

23. A process for the production of an antiperspirant composition comprising, concurrently or in any order, the steps of

15

- incorporating a structurant into a water-immiscible liquid carrier

- mixing the liquid carrier with a disperse liquid phase which is a solution of an antiperspirant active in water, optionally including a water-soluble solvent

20

- heating to an elevated temperature at which the structurant is soluble in the water-immiscible liquid carrier,

followed by

- introducing the mixture into a mould which preferably is a dispensing container, and then

25

- cooling or permitting the mixture to cool to a

temperature at which it is thickened or solidified.

24. A method for preventing or reducing perspiration on  
human skin comprising topically applying to the skin a  
5 composition according to any one of claims 1 to 19.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 00/01230

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61K7/32

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 265 878 A (KEIL JOSEPH W) 5 May 1981 (1981-05-05) claims 1-5 ---	
A	US 4 704 271 A (HOURIHAN JOSEPH C ET AL) 3 November 1987 (1987-11-03) claims 1-7 ---	
A	US 4 719 103 A (KREVALD HELGA ET AL) 12 January 1988 (1988-01-12) claims 1-5 ---	
A	US 4 725 431 A (HOURIHAN JOSEPH C ET AL) 16 February 1988 (1988-02-16) claims 1-5 ---	
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

24 July 2000

Date of mailing of the international search report

01/08/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Stienon, P

# INTERNATIONAL SEARCH REPORT

Inter national Application No

PCT/GB 00/01230

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 291 334 A (UNILEVER PLC ;UNILEVER NV (NL)) 17 November 1988 (1988-11-17)  cited in the application  abstract; claims 1-10; example 1  -----</p>	

**THIS PAGE BLANK (USPTO)**

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/GB 00/01230

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4265878 A	05-05-1981	BE 879717 A BR 7907210 A CA 1125175 A DE 2940908 A FR 2458284 A GB 2050163 A,B IT 1126347 B JP 1139913 C JP 55164618 A JP 57028682 B NL 7907374 A	30-04-1980 27-01-1981 08-06-1982 11-12-1980 02-01-1981 07-01-1981 21-05-1986 24-03-1983 22-12-1980 18-06-1982 09-12-1980
US 4704271 A	03-11-1987	NONE	
US 4719103 A	12-01-1988	NONE	
US 4725431 A	16-02-1988	NONE	
EP 0291334 A	17-11-1988	AT 94054 T AU 597822 B AU 1608988 A BR 8802347 A CA 1325776 A DE 3883838 D DE 3883838 T ES 2059518 T JP 1799931 C JP 5009405 B JP 63303918 A US 4948578 A ZA 8803407 A	15-09-1993 07-06-1990 17-11-1988 13-12-1988 04-01-1994 14-10-1993 20-01-1994 16-11-1994 12-11-1993 04-02-1993 12-12-1988 14-08-1990 31-01-1990